Development Studies of a Novel Wet Oxidation Process[1]

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Needs

Waste streams and remediates containing simple mixtures of components are often easily treated due to their predictability. However, many waste streams from both the federal complex and privately-owned waste generation and remediation sites contain complex and variable mixtures of hazardous organic compounds, toxic metals, and radionuclides that are impractical to characterize completely. These contaminant materials are often found in complex organic and/or inorganic matrices, such as debris, rubbish, used personal protective equipment, various sludges and mixed solids, and some soils and waters. Incineration and similar thermal processes do not appear to be viable options for treatment of these waste streams in many locales due to various considerations. There is a need for a process with a broad application range, that can treat the large majority of complex wastes with a minimum of prior characterization. The non-combustion process should also be safe, effective, cost-competitive, permittable, and preferably mobile.

Objectives

The objective of the effort described here is to develop a novel catalytic chemical wet oxidation process that can be used to effectively treat multi-component wastes with a minimum of pretreatment characterization, thus providing a versatile, non-combustion method which will destroy hazardous organic compounds while simultaneously containing and concentrating toxic and radioactive metals for recovery or disposal in a readily stabilized matrix.

Approach

Although the DETOX^{SM} process had been tested to a limited extent for potential application to mixed wastes, there had not been sufficient experience with the process to determine its range of application to multicomponent waste forms. The potential applications of the process needed to be better identified. Then, the process needed to be demonstrated on wastes and remediate types on a practical scale in order that data could be obtained on application range, equipment size, capital and operating costs, effectiveness, safety, reliability, permittability, and potential commercial applications of the process. The approach for the project was, therefore, to identify the potential range of applications of the process (Phase I), to choose demonstration sites and design a demonstration prototype unit (Phase II), to fabricate and shakedown the demonstration unit (Phase III), then finally to demonstrate the process on surrogate hazardous and mixed wastes, and on actual mixed wastes (Phase IV).

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[1] Research sponsored by the U.S. Department of Energy's Morgantown Energy Technology Center, under Contract DE-AC21-92MC29107 with Delphi Research, Inc., 701 Haines Avenue NW, Albuquerque, NM 87102; telefax: 505-243-3188.

Project Description

Technology:

The DETOX[SM] process uses a unique combination of metal catalysts to increase the rate of oxidation of organic materials. The process has been patented by Delphi Research, Inc. in the U. S. and several foreign countries. The catalysts are maintained in a salt-loaded water solution at 423.-473. K and 100.-700. KPa. Wastes are introduced into the solution, where their organic portion is oxidized to carbon dioxide and water.

The sulfur in sulfur compounds is oxidized to sulfate. Phosphorous in phosphorous compounds is oxidized to phosphate. Chlorine in any form is converted to HCl or chloride salt. Inorganic ammonia will remain as ammonium ion. The nitrogen in organic nitrogen compounds appears to be converted to nitrogen gas. Nitrates (including nitric acid) are eventually reduced to nitrogen gas, but in the process part can escape the process as NO_X. Cyanide is strongly complexed by the catalyst solution and eventually oxidized. There are limits to how much cyanide can be introduced into the catalyst solution at one time.

Many metals will dissolve to some extent in the catalyst solution. This property of the solution can be used to remove toxic and radioactive metals from larger amounts of more inert inorganic material. Since the catalyst solution keeps metals in the ionic state, one does not have to be as concerned with escape of volatile metals such as mercury and cadmium. Many metals can be concentrated in the catalyst solution, if desired, for eventual disposal or recovery. The catalyst solution can be reduced to an iron oxide matrix by boiling off hydrogen chloride and water. The iron oxide matrix can be stabilized by one of a number of methods, preparatory to ultimate disposal of inorganic contaminants.

Schedule and Milestones:

FY95-FY98 Program Schedule

	FY95		FY96				FY97				FY98			
	3rd Qtr.	4th Qtr.	1st Qtr.	2nd Qtr.	3rd Qtr.	4th Qtr.	1st Qtr.	2nd Qtr.	3rd Qtr.	4th Qtr.	1st Qtr.	2nd Qtr.	3rd Qtr.	4th Qtr.
Fabrication														
Shakedown Testing														
Cold Testing														
Unit Mod/Inst														
Hot Testing														

Project Effort

Phase I - In Phase I, destruction efficiencies were measured for six organic compounds, the fates of representative metals in the catalyst solution were determined, the ability of the catalyst solution to treat contaminated soils was established, and a conceptual design for a field demonstration unit was performed.

Phase II - In Phase II, a demonstration site selection survey was conducted and detailed engineering design for a modular, skid-mount demonstration unit was performed.

Phase III - Phase III, now ongoing, is preparation of a Demonstration Test Plan (DTP), and permitting, safety analysis, fabrication and shakedown testing of a prototype unit.

Phase IV - Phase IV will be demonstration of the process on a variety of surrogate hazardous materials at SRS and on a variety of low-level mixed wastes at RFETS.

Results

Phase I:

The DETOX^{SM} process was found to be capable of destroying organic compounds with good efficiency, solvating many toxic metals, and removing organic compounds and toxic metals from soils. The results of Phase I were presented at the 1994 METC meeting.

Phase II:

Sites selected for demonstration were Savannah River Site (SRS) and Weldon Spring Site Remedial Action Project (WSSRAP). A Title II design for the demonstration unit was completed. The results of Phase II were presented at the1994 METC meeting.

Phase III:

Demonstration Test Plan - The DTP gives the project plan, schedule, and the organization by which the project plan will be accomplished. The DTP is considered to be a living document, and refinements continue to be added with the Primary Stakeholders' approval.

A DTP has been completed following guidance supplied by METC, and was approved by the Primary Stakeholders in the demonstration effort. The details of the DTP were presented at the 1995 METC meeting.

Revision 3 of the DTP was completed in November 1995 and approved by the Primary Stakeholders in early January 1996. In January 1996, WSSRAP removed itself from the demonstration effort due to obtaining permission to ship its mixed wastes to Oak Ridge National Laboratory for incineration. Rocky Flats Environmental Technology Sits (RFETS) was chosen as the replacement for WSSRAP. Due to the site change for demonstration on mixed wastes, Revision 3 of the DTP was not issued, as it was already outdated. Revision 4, which includes changes reflecting the site change for demonstration on mixed wastes, is now being completed and is expected to be issued to the Primary Stakeholders for review shortly. The revisions do not affect the shakedown testing at Savannah River Site.

Permit Process and NEPA Documentation - Permitting for the demonstration unit is being pursued for both the demonstration sites. A viable plan has been formulated for each site. Delphi has received a letter from EPA stating that the DETOX^{SM} process unit is considered to be a miscellaneous unit for the purposes of permitting under RCRA. This letter indicates that EPA considers the process to be non-thermal for permitting purposes.

After consultation with SRS environmental personnel and representatives of South Carolina Department of Health and Environmental Control, it was determined that the permitting route to pursue for the demonstration at the TNX facility was to obtain an approval from SCDHEC to operate the demonstration unit as a wastewater treatment unit under the clean water act. This approach required preparation of estimates of water effluent for the demonstration unit during the demonstration. The effluent from the demonstration unit will meet the requirements of NPDES after treatment in the TNX facility's Organics Removal Facility (ORF). The approval letter has been obtained. Estimates of air emissions have also been submitted. The demonstration unit has been granted an air permit exemption based on these estimates. A determination has been made that the demonstration at SRS can be conducted under a NEPA Categorical Exclusion (CX). Delphi has supplied information to SRS and filled out SRS's Environmental Evaluation Checklist to support the CX. NEPA approval at SRS has been given.

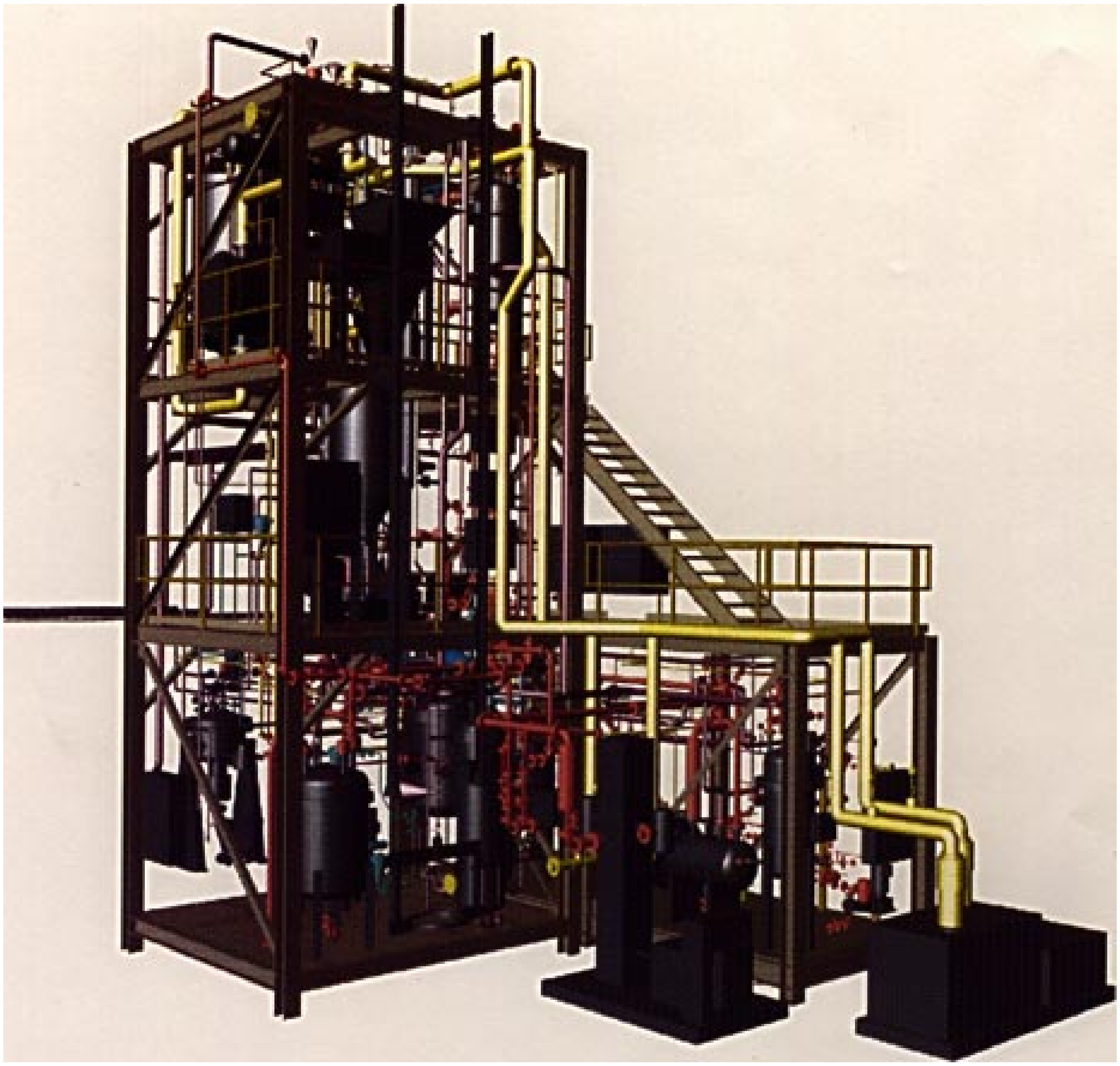
At Rocky Flats Environmental Technology Site (RFETS), a RCRA RD&D permit will be required for the demonstration on mixed wastes. The permit application is approximately 80% complete, lacking only final details from RFETS as to unit placement and installation. An air emissions permit exemption will also be pursued at RFETS. NEPA documentation is also being prepared for this site. The demonstration project should fall under a categorical exclusion at RFETS.

Engineering Design and Fabrication - Title III design is complete and the unit modules have been delivered to SRS's TNX facility. The engineering design details were presented at the 1995 METC meeting.

Delivery schedules for exotic alloy equipment were longer than had been estimated, resulting in a delay of several months in completing fabrication of the prototype unit. The total number of modules also increased from three to four due to breakout of the motor control center (MCC) as a separate module. A picture of the main process modules (Modules 1 and 2) is shown in Figure 1. The two process modules are installed in a containment (generally a diked area) for spill control. Module 3 (not shown) is the oil heating/cooling module, placed external to the process modules containment. Also not shown is Module 4, the MCC, also placed external to the process modules containment. In addition to the four process modules, there is a control/laboratory trailer.

Operations and Safety Analysis - Aspects of the operations and safety analysis were presented in the 1995 METC paper. Testing at Sandia National Laboratories identified the flammability/explosivity limits for organic/oxygen/steam mixtures as expected in the headspace of the prototype unit's primary reaction

Figure 1



vessel, so that those conditions may be avoided. A formal HAZOP of the prototype unit was conducted as per Process Safety Management requirements.

The University of New Mexico's Chemical and Nuclear Engineering Department has conducted steady state and dynamic simulations of the prototype unit to identify operating conditions for the unit and the response of the unit to potential upset conditions. These studies have identified the upset scenarios likely to cause problems, the heating and cooling times, the water/HCl balance in the overhead system, and the necessary response times for the control loops.

Argonne National Laboratory has investigated the use of a chemically bonded phosphate ceramic (CBPC) waste form to stabilize the DETOX^{SM} solution residue. Samples of the ceramic have been prepared using simulants of the solution residue loaded with lead and mercury, and ferric phosphate solids loaded with lead and mercury. The samples show good physical strength and are non-hazardous for lead and mercury by the standard EPA Toxicity Characteristic Leaching Procedure (TCLP). The phosphate ceramic also had leach rates comparable to glass forms for lead, mercury, and the radionuclide simulants cesium and cerium, during extended leaching studies as per ANS 16.1 and MCC 1-P.

Personnel at SRS have conducted a Process Hazards Review (PHR) to determine the safety requirements for the demonstration. Recommendations from this review will be incorporated in the demonstration project at SRS.

Additional DETOX^{SM} solution chemistry and physical property studies were stimulated by comments from the Mixed Waste Focus Area. Of concern were the solubilities of common inorganic species in the process solution and their effect on the process solution's physical properties (such as density, viscosity, and surface tension), and the filterability of the iron oxide residue from the process solution. These studies showed that the solubility of most common inorganics in the process solution was limited, and that no large changes in physical properties occurred, even when the entire range of inorganics were introduced into the process solution simultaneously. There are changes in the physical properties, and these may be useful in determining the extent of buildup of common inorganic species in the process solution. It was known that the iron oxide residue from the process solution could be filtered, but it was also known that the filtration process was fairly slow, and was apt to be exacerbated by the presence of soluble inorganics buildup in the process solution. In a series of studies, an innocuous agglomeration agent was found which would double or more than double the filtration rate for the iron oxide residue at only 5 - 10% by weight loading. This agglomeration agent may be used in the demonstration.

In addition to the inorganic chemistry studies, a series of materials compatibility studies were conducted to determine the suitability of various gasket and containment coating materials, and to gather more data on the corrosion rates of tantalum and titanium under the process conditions, especially in the presence of process solution saturated with a variety of likely soluble common inorganic species (such as fluoride, nickel, aluminum, sodium, calcium, sulfate, phosphate, and zinc). The studies identified a very resistant gasket material for use in process lines carrying DETOX^{SM} solution, and established the excellent compatibility of tantalum and titanium under the expected process conditions over more than 1000. hours of exposure.

Benefits

The DETOX^{SM} process is a viable alternative to incineration and similar high temperature or combustive-type processes for the treatment of organic mixed wastes. It has advantages over other processes in its ability to contain metals.

Because the process is conducted at relatively low temperatures and pressures, its emissions are more easily controlled than many thermal treatment processes. This gives advantage not just in operations, but in permitting.

The DETOX^{SM} process can destroy a wide variety of organic materials, and treat many waste matrices, making it versatile in application. The DETOX^{SM} solution's ability to solvate toxic and radioactive metals allows separation of these metals from inert materials in a waste stream. Although some small amount of radioactive material will almost always remain in the inert portion, it will no longer be a mixed waste, and if the input waste was TRU the inerts will in many instances be sufficiently low in radioactivity to be low-level waste only. Careful monitoring of the DETOX^{SM} solution when processing TRU waste can also assure that the process solution residue is low-level only, if desired.

Estimated costs for waste treatment using the process range from $2.50/kg to $25.00/kg, depending on the size of the unit and the amount of waste processed. Estimated cost of waste treatment with the 25. kg (dry weight, organics) demonstration unit is $9.40/kg (dry weight, organic). Process units can be mobile for on-site treatment of wastes.

Future Activities

The demonstration unit is being installed at Savannah River Site's TNX facility, and will be tested for functionality using mineral oil and combustible organic solids. These tests will establish the suitability of the unit for treatment of surrogate hazardous wastes.

Phase IV is the planned demonstration of the unit on surrogate hazardous and mixed wastes and then on actual mixed wastes. Phase IV demonstration at SRS will use surrogate hazardous wastes only, to evaluate the performance of the demonstration unit in a non-radioactive setting. The unit will treat an assortment of surrogate hazardous and mixed wastes including oil loaded with mercury and lead, oil/contaminated water mixture, non-halogenated solvents, halogenated solvents, chlorinated oil, scintillation fluid, railroad ties, and combustible solids loaded with naphthalene, chlorobenzene, dichlorobenzene, cerium, neodymium, and perhaps some heavy metals. After the surrogate hazardous waste experimental campaign, the unit will be cleaned, inspected, modified, and transported to RFETS. This will demonstrate transportability of the unit. At RFETS, the unit will be installed, operationally checked out with non-radioactive feed material, and then used to treat a variety of low level mixed wastes including contaminated oils and solvents, excess chemicals, paints and sludges, solidified organics, PCB wastes, and combustible solids.

A commercialization assessment will be performed during Phase IV of the demonstration, which will include conceptual design of a baseline commercial process unit and sensitivity analysis for factors affecting performance and cost. Following the demonstration, a determination will be made as to the disposition of the unit and its possible future use at RFETS or other sites.

Acknowledgments

We would like to thank EM-50, and in particular Paul Hart, William Schutte, James Taylor, and Allison Johnson, for their support and assistance in making this project possible. We would like to acknowledge the excellent assistance and support provided by METC and the CORs assigned to the project, V.J. Kothari, James Westhusing, Keith Westhoff, and our current COR, William Huber. We would also like to acknowledge the excellent assistance provided by Energetics, in particular Alan Brown, Roger Wetzel, and Chris Wyatt. We would like to acknowledge the contributions of the Sandia National Laboratories Explosives Group, that has performed the flammability simulations and testing, Argonne National Laboratory, that has performed the work on the chemically bonded phosphate ceramic final waste form for the DETOX^{SM} solution residue, and The University of New Mexico Chemical and Nuclear Engineering Department, that has performed steady state and dynamic simulations of the prototype unit. We would also like to acknowledge the help and assistance we have obtained from the DOE and M&O personnel at Savannah River Site and Rocky Flats Environmental Technology Site, especially George Mishra, Karen Azzaro, Beverly Skwarek, Steve Sheetz, Mark Fachada, Lynn Martin, Bill Paine, Carl Cook, Marie Berry, Nancy Turner, David Boyce, Frank Lustig, Gary Huffman, Linda Bateman, John McFee, Jeff Petersell, Barbara Krogfuss, Charles Brown, and Beth Fabrizio. The period of performance for the contract is September, 1992 to September, 1998. The work being performed falls under the review of the Mixed Waste Focus Area. We would like to thank Dirk Gombert, Bill Owca and Dave Valentich for their insightful comments and suggestions.